NASA-CR-203723

01900

THEORETICAL STUDIES OF IMPORTANT PROCESSES IN PLANETARY AND COMET ATMOSPHERES

Status Report and Renewal Request

February 1, 1996 - January 31, 1997

NASA Grant NAGW 1404

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This report is a brief summary of research supported under NASA Grant NAGW 1404 during the period 2/1/96-1/31/97. Also included is a renewal budget for the period 2/1/97-1/31/98.

A. Progress Under NASA Grant NAGW 1404

We have continued our theoretical calculations on the dissociative recombination (DR) of O_2^+ with an electron, $O_2^+ + e^- \rightarrow O + O$. During the past year we have focused upon the generation of excited $O(^1D)$ and $O(^1S)$ atoms. In order to determine accurate rate constants for this process it is important to have accurate potential curves that describe the nuclear motion. Our prior work has shown that three states of O_2 ($f'^1\Sigma_u^+$, $B^3\Sigma_u^-$, and $1^1\Delta_u$) control the generation of excited atoms from the low vibrational levels of the O_2^+ ground state. Using state of the art techniques during the past year, we have determined highly accurate potential curves for these three states using large scale configuration interaction (CI) wave functions and contracted [5s,4p,3d,2f,1g] Gaussian basis sets. For the $B^3\Sigma_u^-$ state, the calculated (experimental(Krupenie, 1972)) ω_e, $\omega_e x_e$, R_e, D_e, and T_e are 721.0cm^{-1}(709.057cm^{-1}), 13.02cm^{-1}(10.61408cm^{-1}), 3.0311a$_0$(3.03165a$_0$), 1.2376eV(1.007eV), and 6.2379eV(6.1737eV). The result for R_e is among the most accurate results ever calculated for a molecule of this size. These results indicate that the shape of the B state potential curve is quite close to experiment. Results of comparable accuracy have also been obtained for the ion ground state indicating that the B state is accurately located relative to the ion. For $^1\Delta_u$, there are no experimental results for comparison to our calculations. For $^1\Sigma_u^+$, there has been a recent determination (B. R. Lewis et al., 1995a) of the dissociation energy and the excitation energy. For D_e and T_e the calculated (experimental) values are 1.1852eV(1.35eV), and 10.087eV(10.02eV). These results are of comparable accuracy to the $^3\Sigma_u^-$ results. We can expect that the $^1\Delta_u$ results are also of comparable accuracy.

The DR cross sections and rates are approximately directly proportional to an electron capture width, Γ, calculated as the matrix element of the Hamiltonian, H, between two diabatic states describing P and Q space,

$$\Gamma = 2\,\pi\,\rho\,|<\Psi_P\,|\,H\,|\,\Psi_Q>|^2$$

where ρ is a density of states. Ψ_P is the space of Rydberg states and Ψ_Q is the dissociative state.

High Rydberg states are used to model the electron-ion continuum and calculate free electron capture widths. The widths are determined by first calculating the CI wave functions for the dissociative states. High, non-physical roots in the dissociative space are allowed to mix into the Rydberg space in order to provide additional correlation for the Rydberg space. Our previously calculated widths (Guberman, 1988) were calculated to a distance of $3.0a_0$. However, once we extended the calculations to slightly larger distances, we found that charge transfer routes from the Q space caused an unphysical variation of the width with internuclear distance at these large distances. These routes were removed from P space. The new widths differ from our previously calculated widths (Guberman, 1988) by less than 10%. Recent experimental determinations of these widths are in excellent agreement with our calculated values. Detailed line width measurements (B. R. Lewis et al., 1995a) show that the n=3 $f'^1\Sigma_u^+$ Rydberg state has a matrix element with the $f'^1\Sigma_u^+$ state of 1500-2000cm^{-1} at R=$2.532a_0$. For comparison, we have calculated the matrix element for n=3 at $2.5a_0$. Our calculated value is 1698cm^{-1} and is in excellent agreement with the experimentally derived range. For $^3\Sigma_u^-$, our calculated n=3 matrix element at R=$2.2819a_0$ is 4319cm^{-1} and is in excellent agreement with an experimentally derived value (B. R. Lewis, 1995b) of 4038cm^{-1}. The derivation of the experimental value assumed that the calculated matrix element is R independent in the Franck-Condon region and this is supported by our results which show an insignificant R dependence in this region. There are no experimental values to compare to the calculated $^1\Delta_u$ width.

The widths calculated above, especially that for $^3\Sigma_u^-$, are the largest widths (with the exception of O_2 $^3\Pi_u$ and $^1\Pi_u$) that have been calculated in this laboratory to date. The Multichannel Quantum Defect Theory (MQDT) approach (S. L. Guberman and A. Giusti-Suzor, 1991) which we have used for the calculation of DR rates must be revised to handle these large widths and this revision is discussed in the next section. In a recent paper (S. L. Guberman, 1996), we described a new mechanism by which vibrationally excited Rydberg states can couple together dissociative routes of the same symmetry leading to a large increase in the cross section from the DR route with the lower DR cross section. We believe that this mechanism may play a role even when dissociating routes have different symmetries. This mechanism and its application to DR along the $^1\Sigma_u^+$ channel of O_2 is described in the next section.

B. Plan of Work for the Period 2/1/97-1/31/98

The calculated DR rate from the v=0 ion level along the $^1\Sigma_u^+$ channel at an electron temperature of 300K is 0.6 x 10^{-10}cm^3/sec. This rate is more than three orders of magnitude smaller than the calculated rate along the $^3\Sigma_u^-$ dissociative route. In the prior section we mentioned that we have recently described a new DR mechanism in which dissociative routes of the same state symmetry can mix together via excited vibrational levels of Rydberg states of that symmetry. By "mix together" we mean that the dissociative flux along one channel can leak into another dissociative channel. However, in O_2, the $^1\Sigma_u^+$ dissociative channel is the only state of its symmetry arising from neutral atoms. Nevertheless, the same mechanism can occur if the Rydberg states of $^1\Sigma_u^+$ symmetry can mix with Rydberg states of another symmetry (say $^3\Sigma_u^-$) by spin-orbit coupling. In this manner, the seemingly weak $^1\Sigma_u^+$ DR channel can mix with the stronger $^3\Sigma_u^-$ channel. Only a small amount of mixing is needed in order to make a very big change in the $^1\Sigma_u^+$ rate. In this mechanism, the incoming electron would be captured into the $^3\Sigma_u^-$ dissociative state or directly into $^3\Sigma_u^-$ Rydberg states. A small amount of this incoming flux would then leak out into $^1\Sigma_u^+$ Rydberg states through the spin-orbit coupling between $^3\Sigma_u^-$ and $^1\Sigma_u^+$ Rydberg states. The $^1\Sigma_u^+$ Rydberg states are coupled to the $^1\Sigma_u^+$ exit channel leading to O(^{1}S) atoms. This mechanism can resolve the long standing mystery of why some experiments have detected nonnegligible yields of O(^{1}S) from DR of O_2^+ but theory clearly shows that the $^1\Sigma_u^+$ dissociative route does not cross the v=0 ion level and has a very low DR rate constant. The spin orbit coupling term between these two Rydberg series has recently been estimated to be 96cm^{-1}(B. R. Lewis et al., 1995b) and is independent of the Rydberg principal quantum number. We propose to study this mechanism using the MQDT approach that we are currently using for the calculation of DR cross sections and rate constants. We have previously revised the MQDT approach to handle a mixing matrix which accounts for the mixing of electron partial waves due to the cylindrical symmetry of the molecule. This approach can also be used to include spin orbit coupling in the rate constant calculations.

In the MQDT approach (S. L. Guberman and A. Giusti-Suzor, 1991) for calculating the DR rate constants, a K matrix is used which contains all the interactions among dissociative states and excited Rydberg vibrational levels. This matrix is given by the Born expansion of the Lippmann-Schwinger equation, K = V + VGK, where G is the standing wave Green operator and

V is the potential that couples the dissociative and electron-ion states. This matrix is generally calculated to second order. Because of the very large widths calculated for the $^3\Sigma_u^-$ dissociative state (and for the $^3\Pi_u$ and $^1\Pi_u$ states) we propose to begin the study of the nonperturbative calculation of the K matrix using an algebraic technique. This technique has already been applied to atoms (P. L. Altick and E. N. Moore, 1966) and will be included in our MQDT program.

We also propose to begin the calculation of potential curves for the description of the DR of CO^+. Excluding dissociative routes of quintet spin symmetry and of Σ^- and Φ symmetry which are symmetry forbidden as DR routes for the ion $^2\Sigma^+$ ground state, there are 23 possible dissociative routes. We will begin by doing small scale CI calculations in order to survey the states and determine which potential curves provide likely DR routes. Both the ion ground state and the likely DR routes will be calculated in large scale CI calculations. Because CO has fewer electrons, these calculations are expected to give even more accurate results than those reported above for O_2.

C. References

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D. Publications Acknowledging NASA Support (2/1/96-1/31/97)

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